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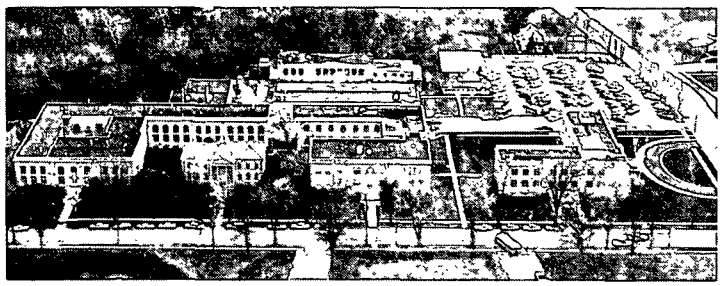

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 110

MASS SPECTRA OF QUINONEMETHIDE PRODUCTS DERIVED FROM REACTION WITH PHENOLICS, ANTHRONE AND ANTHRAHYDROQUINONE

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MARCH, 1981

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GENERAL SUMMARY

The following paper, which was submitted to the Journal of Wood Chemistry and Technology, is an outgrowth of work done on Project 3475-2 (formally 3370). The project is concerned with developing a fundamental understanding of the chemistry of delignification. Mass spectroscopy (MS) and gas chromatography (GC)-MS have been extensively used to characterize pure products and complex mixture obtained in this project's work.

The paper organizes our extensive MS data into a single place and provides an indepth interpretation of the mass spectra of two classes of compounds, model lignin condensation products and model lignin-anthrahydroquinone reaction products. These compound classes exhibit predictable behavior inside the mass spectrometer; a behavior which should extend to more complex molecules having similar structures. The data provides a resource of knowledge to aid in future mass spectral studies, such as the analysis of pulping liquors by GC/MS.

We also discuss how a commonly employed derivatization procedure, namely methylation with dimethylsulfate in tetrahydrofuran, gives rise to undesirable by-products.

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ABSTRACT

Several experiments have been performed to show the effects of anthrahydroquinone (AHQ), the reduced form of anthraquinone (AQ), on the self-condensation reactions of simple lignin models. These experiments were aimed at understanding the role of AQ as a wood pulping catalyst. The experiments led to some very complex product mixtures. A detailed analysis of the product mixtures by gas chromatography - mass spectrometry (GC/MS) was undertaken in order to understand how AHQ retarded phenolic-quinonemethide condensation reactions. The interpretation of the mass spectra is reported here. Two principal classes of compounds are discussed: phenolic condensation products and adducts derived from the reactions of quinonemethides with AHQ and anthrone. A method of volatilizing the sample prior to GC/MS analysis, namely derivatization with dimethyl sulfate in alkaline THF, produces by-products which contain incorporated THF.

INTRODUCTION

Gas chromatography - mass spectroscopy (GC-MS) is an extremely useful technique for detecting trace components in complex mixtures and providing information as to the nature of the components. Modern instruments generally have a data base of "library" spectra, which can be searched in an attempt to provide a match with a sample spectrum. For unique samples, the library searching routine, at best, provides only clues as to possible structural features. One is then left with deducing reasonable

structures from the molecular ions and fragmentation ions observed in the spectra.

In the previous paper,[1] we discussed briefly the characterization of vanillyl alcohol condensation products by GC-MS. The library searching routine was not very successful in this case and structures were principally deduced from fragmentation patterns and molecular weight determinations. We would like to discuss here our spectral interpretations, hoping that this information may also prove valuable to the interpretation of mass spectra of wood pulping components having similar structures. The main focus of this report centers around three classes of compounds: (1) the condensation products of vanillyl alcohol, a simple lignin model, (2) the addition products obtained from anthrahydroquinone (AHQ) reacting with quinonemethides (QMs) and (3) the by-products of derivatizing with dimethyl sulfate (Me_2SO_4) in alkaline tetrahydrofuran (THF).

RESULTS AND DISCUSSION

Condensation Products

Phenolic dimers, trimers, and tetramers have been generated from the alkaline reactions of vanillyl alcohol (1) and p-hydroxybenzyl alcohol (2) or precursors of these, namely chloroacetates 3 and 4.[1] Potential intermediates in these reactions are quinonemethides 5 (from 1 or 3) and 6 (from 2 or 4). Product mixtures were derivatized with Me_2SO_4/NaOH/THF to give the more volatile methyl ethers and then analyzed by GC-MS. The derivatization procedure often gave THF by-products (to be discussed later) and partial methylation of alcoholic hydroxyl groups.

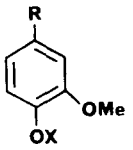
Besides methylation of known samples, the principal source of the compounds under discussion were derived from methylation of the products obtained from the reactions outlined by equations a-e below. The detailed chemistry behind these reactions is discussed elsewhere;[1-3] therefore only a brief discussion will be given here.

The reaction described by equation a generates phenolic condensation products via intermediate quinonemethide 5.[2] The conditions of equation b generate a quinonemethide of 7 which then either attacks anthrone 8 or condenses.[3] The reactions described by equations c-e have a common feature; adduct 9 is known to fragment at temperatures above 60°, generating anthrahydroquinone dianion (AHQ^{-2}) and quinonemethide 6. Therefore, equation c depicts a reaction of AHQ^{-2} with quinonemethides 6 and 5 (from 3) giving rise to mixed adducts and condensation products.[3] 3,5-Dinitrobenzoic acid rapidly converts AHQ^{-2} to anthraquinone (AQ); thus, the products of equation d are principally condensation products of 2 and 6.[3] Reduction products are observed in the reaction outlined by equation e.[3]

Table I presents the important signals seen in the mass spectra of some simple monomers done by the electron impact (EI) and chemical ionization (CI) techniques. The table and subsequent ones do not list signals that are obviously just ^{13}C-isotope analogs of the species one unit lower in weight. The term Me in the source column of the table signifies methylation by $Me_2SO_4/OH^-/THF$.

TABLE I

Mass Spectral Data for Monomers

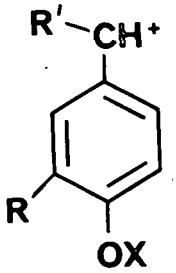


Compound	Source	X	R	Mol. Wt.	Type	m/e (%)
1	Commerc.	H	$-CH_2OH$	154	EI	154(100) 137(45) 93(77) 65(82)
					CI	155(25) 154(15) 153(19) 137(100) 125(28)
10	Me of 1	Me	$-CH_2OH$	168	EI	168(100) 151(26) 139(36) 138(25)
					CI	169(42) 168(13) 167(13) 151(100) 139(14)
11	Me of 1	Me	$-CH_2OMe$	182	EI	182(47) 181(11) 151(100)
					CI	183(26) 182(13) 181(5) 151(100)
13	Me of 12	Me	$-CHO$ OH	166	EI	166(100) 165(61) 95(21) 77(16)
					CI	167(100) 166(8) 165(2) 151(12)
14	Rx b	Me	$-CHCH_3$	182	EI	182(42) 180(48) 167(54) 165(100) 139(48)
					CI	183(40) 182(21) 181(100) 165(61) 139(24)
15	Me of 1	Me	$-CH_2O(CH_2)_4OMe$	254	EI	254(42) 167(80) 151(100) 87(52) 45(28)
					CI	255(1) 254(4) 151(100)
16	Me of 12	$-(CH_2)_4OMe$	$-CHO$	238	EI	238(3) 151(20) 87(100) 45(72)

The CI data were obtained using methane as the reagent gas. The "softer" ionization that occurs during CI generally gives rise to large M + 1 signals (equation f), without much fragmentation, thereby pin-pointing the molecular weight of the species.[4,5] Fragment ions can occur in CI by extraction of a functional group (OH, OR, etc.) by a positive ion (equation g) or loss of H_2O, CH_3OH, etc., from the M + 1 species; these can be very important processes when highly stable fragment ions result.

The CI spectra reported in the tables only list the M + 1, M, M - 1, and fragmentations observed. In every case, M + 29 and M + 41 signals were observed, verifying the molecular weight. In general, these were weak signals and were, thus, omitted from the tables. Occasionally, the M + 29 was as strong or stronger than a (weak) M + 1 signal; in these cases we assume that the M + 1 ion was relatively unstable and fragmented to a more stable ion.

In general, both the EI and CI spectra reported in Table I show that these simple compounds give rise to strong molecular ions (M + 1 in the CI case) and benzyl ions. [The term "benzyl" will be used for simplicity sake, when in reality "tropylium" ions are probably the better description.[6]] The derivatives of vanillin (12), namely 13 and 16, are not really "benzyl" type compounds and thus do not show much strength at m/e 151. The typical benzyl ions seen throughout our studies are shown below.



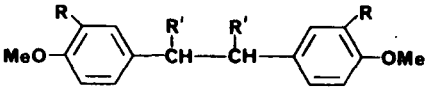
	X	R	R'	m/E
17	H	H	H	107
18	Me	H	H	121
19	H	OMe	H	137
20	H	OMe	Me	151
21	Me	OMe	H	151
22	Me	OMe	Me	165

Many of the monomers, especially 14, displayed reasonably strong M - 1 signals in the CI spectra. The ion responsible for the M - 1 signal is probably an oxygen stabilized benzyl carbonium ion derived from hydroxide extraction (equation 7) of a benzyl hydrogen.

Table II lists the spectra of some head-to-head dimers that were obtained from several reactions. Compound 25a and 25b are erythro, threo isomers. Benzyl ion fragments are very dominant for most of the compounds listed in Table II. The molecular ions also show up well in each case. The CI mode produces two kinds of fragments, namely a symmetrical splitting of the benzyl carbons and a cleavage of a benzyl-aryl bond.

TABLE II

Mass Spectral Data of Head-to-Head Dimers



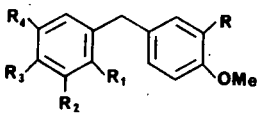
Compound	Source	R	R'	Mol. Wt.	Type	m/e (%)
23	Rx e	H	H	242	EI	242(19) 121(100)
					CI	243(44) 135(100) 121(30)
24	Rx a	OMe	H	302	EI	302(100) 287(30) 271(30) 165(20) 151(13)
					CI	303(100) 302(23) 301(12) 165(50) 151(96)
25a	Rx b	OMe	Me	330	EI	330(11) 165(100) 150(5)
					CI	331(74) 330(21) 329(12) 193(100) 165(40)
25b	Rx b	OMe	Me	330	EI	330(8) 165(100) 150(5)
					CI	331(56) 330(20) 329(9) 193(100) 165(31)

Several research groups have studied the self-condensation reactions of vanillyl alcohol (1) and several products have been characterized, mostly as their acetate or methyl ether derivatives.[1,7,8] These compounds correspond to structures 26-31. Table III lists the principal mass spectral signals of a number of phenolic condensation products derived from vanillyl alcohol or p-hydroxybenzyl alcohol (2) or the mixture of the two.

Many of the structual assignments given in Table III are based on chemistry and MS fragmentation patterns analogous to the known vanillyl alcohol system. For example, vanillyl alcohol and alkali yield a major dimer (molecular weight 288) of low GC retention

TABLE III

Mass Spectral Data for Dimer, Trimer, and Tetramer Phenolic Condensation Products



Compound	Source	R	R_1	R_2	R_3	R_4	Mol. Wt.	Type	m/e (%)
26	Ref 1,8	OMe	H	H	OMe	OMe	288	EI	288(100) 257(60) 151(11)
								CI	289(79) 288(10) 287(5) 151(100)
27	Rx a	OMe	OMe	OMe	H	CH_2OMe	332	EI	332(100) 317(11) 301(14) 287(11) 269(13)
								CI	361(11)* 333(8) 332(13) 331(7) 301(100) 195(80) 151(37)
28	Rx a	OMe	CH_2OMe	H	OMe	OMe	332	EI	332(19) 300(15) 269(100) 254(13) 238(22) 151(51)
								CI	333(17) 332(8) 331(5) 301(82) 151(100)
29	Ref 8	OMe	CH_2OH	H	OMe	OMe	318	EI	318(56) 300(23) 269(100) 180(34) 179(21) 151(11)
								CI	
30	Rx a	OMe	OH	OMe	H	CH_2OMe	318	EI	318(36) 152(100) 151(60) 137(25) 121(26)
								CI	347(4)* 319(1) 318(3) 317(1) 151(100)
31	Rx a	OMe	OMe	OMe	H	CH_2Ar'	438	EI	438(100) 423(12) 407(10) 287(21) 151(88)
								CI	**
32	Rx a	OMe	CH_2Ar'	H	OMe	OMe	438	EI	438(20) 287(10) 285(12) 269(100) 254(14) 238(14)
								CI	
33	Rx c	H	H	H	OMe	OMe	258	EI	258(100) 243(8) 227(60) 121(12)
								CI	259(100) 258(20) 257(6) 151(28) 121(27)
34	Rx c	H	OMe	OMe	H	CH_2Ar	378	EI	378(100) 363(30) 347(13) 257(36) 151(17) 121(48)
								CI	
35	Rx c	H	OMe	OMe	H	CH_2Ar'	408	EI	408(100) 393(18) 377(10) 287(16) 257(14) 151(23) 121(48)
								CI	**
36	Rx d	H	H	H	OMe	H	228	EI	228(100) 227(32) 197(63) 121(25)
								CI	229(70) 228(10) 227(7) 121(100)
37	Rx d	H	OMe	H	H	CHO	256	EI	256(100) 241(6) 227(48) 121(47)
								CI	257(100) 256(10) 255(3)
38	Rx d,e	H	OMe	H	CH_2OMe	H	272	EI	272(26) 241(19) 121(100)
								CI	273(11) 121(100)
39	Rx d	H	OMe	H	H	CH_2AR	348	EI	348(100) 317(19) 227(79) 121(48)
								CI	377(5)* 349(6) 348(13) 347(8) 241(100) 121(14)
40 or 41	Rx d	[CH_2Ar]	OMe	[H]	H	CH_2Ar	468	EI	468(76) 360(94) 347(31) 121(100)
								CI	
42	Rx d	[H]	OMe	[CH_2Ar]	H	CH_2OMe	392	EI	392(75) 360(100) 345(22) 271(22) 239(20) 121(99)
								CI	
43	Rx d	[CH_2Ar]	OMe	[H]	H	CH_2OMe	392	EI	392(100) 361(18) 360(12) 359(16) 284(60) 271(23) 253(31) 121(40)
								CI	
44	Rx d	[H]	OMe	[CH_2Ar]	[H]	CH_2OH	376	EI	376(100) 328(25) 255(34) 227(36) 121(69)
								CI	417(90)* 405(28) 377(45) 376(12) 269(100)
45	Rx d	[CH_2Ar]	OMe	[H]	[H]	CH_2OH	376	EI	376(64) 268(100) 267(16) 253(21) 121(30)
								CI	417(37)* 405(22) 377(100) 269(42)
46	Rx a	[H]	OMe	[H]	[CH_2Ar]	CH_2OH	376	EI	376(40) 361(100) 121(44)
								CI	337(100) 269(74)

Code: Ar ≡ p-MeOPh -, Ar' ≡ 3,4-DiMeOPh-, '[ ] ≡ assignments may be reversed, * unusually strong M + 41 or M + 29 relative to M + 1 signal, ** weak spectrum, but displayed signals at M + 1, M + 29, and M + 41 indicative of the proposed molecular weight

time and a minor dimer (mol. wt. 330) of long GC retention time. The alkaline condensation reactions of p-hydroxybenzyl alcohol afford a major, low mass, low retention time dimer and a minor, high mass, high retention time dimer. Since the two starting materials only differ by an aryl methoxyl group, analogous structures were proposed for the dimer products; the mass spectra showed many similarities, too.

Benzyl ions, m/e 121 and/or 151, are present in all the spectra recorded in Table III; they were somewhat more dominating in the CI mode than the EI mode. Reasonably intense signals due to M - 15 (CH_3) and M - 31 (OCH_3) were seen in most of the EI spectra; also, M - 121 or 151 (benzyl) were prominent in the trimers and tetramer spectra.

The spectra of isomer pairs 27/28, 29/30 and 31/32 show remarkable differences, which we believe are related to the interaction of a benzyl substituent with an ortho-methylene. The reactions in Scheme I offer an interpretation of the EI and CI spectra for dimer 28. In the first two stages we propose ionization of a methoxyl oxygen followed by a 6-membered ring transition state loss of methanol. Analogous fragmentations are known to be quite favorable for alcohols. A Cope rearrangement and eventual loss of a methoxyl radical are proposed for the latter stages of the fragmentation process to afford a highly stabilized, "dibenzyl," carbonion ion, m/e 269. The CI spectrum is dominated by a m/e 301 signal, presumably a benzyl ion resulting from either loss of CH_3OH from a M + 1 species or extraction of methoxide by a positive ion in the system.

The m/e 269 fragment is an important signal in the spectra of dimer 29 and trimer 32. This fragment could arise by a process similar to that proposed in Scheme I in which either water (for dimer 29) or an aromatic ring (for trimer 32) is initially eliminated, again via a 6-membered ring transistion state. Dimer 29 was not observed by us in our work and its mass spectrum is the only data in the tables taken from another source.[8]

We observed three dimers of mass 318 from the reaction outlined by equation a; none of these showed a m/e 269 signal in their mass spectra. One of these m/e 318 dimers was assigned a structure, namely 30, based on the unusual appearance of a strong m/e 152 signal in its spectrum; the latter fragment probably arises via a cleavage and transfer of a hydrogen from a phenolic hydroxyl group to an ortho-methylene group. The other two isomers, which show two principal signals at 318 and 151, were found in very small amounts and are probably analogous (less methylated) versions of dimer 27.

The m/e 269 signals which appear in the CI spectra of trimers 44-46 are probably simple benzyl ions resulting from loss of 107 units (PhOMe). Analogous losses of 107 units for 39 and 137 (1,2-diMeOPh) units for 30 are seen in other CI spectra. It is interesting to note that the CI spectra occasionally gave prominent fragments not seen in the EI spectra and, thus, provided additional structural information.

Compounds 33-35 are mixed dimers and trimers produced from two quinonemethides (5 and 6) and two phenols (1 and 2). Dimers 36-38, trimers 39, 42-46 and tetramer 40 or 41 were obtained from the reaction outlined by equation d and Scheme II. The methylation of the trimers containing benzylic alcohol groups gave fully methylated derivatives 42 and 43 and partially methylated derivatives 44-46. The spectra of these trimers 42-43 and 44-46 were quite different from one another but not conclusive enough to assign structures; the structures in Scheme II appear to be likely candidates. The interpretation here was also complicated by the low levels of these trimers in the sample and the occurrence of some GC retention time overlap.

QM-AHQ Adducts

Anthrahydroquinone (AHQ) reacts with quinonemethides (QM's) to give addition products, known as QM-AHQ adducts.[1,9,10] These compounds may be important in explaining the rapid delignification rates which accompany the pulping of wood with anthraquinone as a

catalyst.[1,2,9-11] Several articles have been directed at determining the fate of AQ during pulping;[12-19] MS and GC/MS will probably play a major role in providing structural information for the characterization of the trace reaction products derived from AQ.

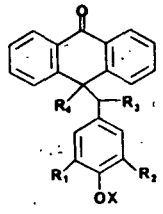
Table IV presents the mass spectral data for a number of QM-AHQ adducts which we have observed in previous work.[13] The underivatized compounds (X = H, Table IV) have been extensively characterized by other means;[2] because of relatively low volatilities, these compounds were directly inserted into the source by a direct insertion probe in order to obtain their mass spectra. Except for 64-66, the remainder of the compounds reported in Table IV were produced by simple derivatization of known compounds with $MeSO_4/OH^-/THF$. The main products of the derivatization were generally the fully methylated analog, but some partially methylated and THF incorporated products were frequently observed in small amounts.

One of the most prominent fragmentations observed in the EI spectra of the adducts was cleavage of the C_{10}-benzyl bond: (eq. h) The only time when significant ions were observed (EI mode) from cleavage of the other C_{10}-substituent (R_4) was when R_4 = methyl or $O(CH_2)_4OMe$. Molecular ions were not overly strong (EI mode) unless the R_4 substituent was methyl (48 and 51) or $-CH_2Ar$ (52).

The CI mode for the adducts tended to produce large amounts of benzyl ions (69); generally the benzyl signal was the base peak. The strength of the signals associated with the molecular ion in the CI mode, i.e., M, M + 1, M + 29, and M + 41, varied considerably from one compound to the next. The aryl ions associated with 68 were generally weak or nonexistent in this mode. Signals associated with loss of the R_4 substituent were often observed in the CI mode; examples are M-17(OH) for 54, 55, 59, and 63, M - 31 (OMe) for 56 and 60, M - 103 ($OCH_2CH_2CH_2CH_2OMe$) for 57 and M - 59 (OAc) for 58.

TABLE IV

Mass Spectral Data for Adducts of Quinonemethides and Anthrahydroquinone or Anthrone



Compound	Source	R_1	R_2	R_3	R_4	X	Mol. Wt.	Type	m/e (%)
47	Rx d[3]	H	H	H	H	H	300	EI	300(2) 194(100) 193(10) 165(14) 107(16)
								CI	301(100)
48	Me of 47	H	H	H	Me	Me	328	EI	328(100) 313(86) 121(16)
								CI	
49	Ref 3	H	OMe	Me	H	H	344	EI	344(1) 194(35) 193(18) 165(41) 151(100) 91(34)
								CI	345(100) 179(20) 151(85)
50	Me of 49	H	OMe	Me	H	Me	358	EI	358(1) 194(3) 193(2) 165(100) 150(7)
								CI	359(1) 358(1) 357(1) 165(100)
51	Me of 49	H	OMe	Me	Me	Me	372	EI	372(100) 357(48) 165(13) 151(45)
								CI	
52	Ref 3	H	H	H	p-HOPhCH$_2$	H	406	EI	406(22) 300(100) 208(46) 194(57) 121(25) 107(60)
								CI	301(4) 223(2) 209(1) 135(8) 107(100)
53	Me of 52	H	H	H	p-MeOPhCH$_2$	Me	434	EI	434(2) 313(4) 241(8) 121(100)
								CI	435(19) 121(100)
54	Ref 2	H	H	H	OH	H	316	EI	316(1) 210(100) 209(33) 181(15) 152(33) 107(27) 77(25)
								CI	317(81) 299(7) 210(10) 209(18) 195(8) 135(10) 107(100)
55	Me of 54	H	H	H	OH	Me	330	EI	330(0.4) 209(32) 152(14) 122(35) 121(100)
								CI	331(12) 313(12) 209(27) 122(19) 121(100)
56	Me of 54	H	H	H	OMe	Me	344	EI	344(6) 223(54) 152(18) 121(100)
								CI	345(20) 313(23) 121(100)
57	Me of 54	H	H	H	O(CH$_2$)$_4$OMe	Me	416	EI	416(1) 312(54) 311(26) 281(20) 239(18) 121 (44) 87(100) 45(29)
								CI	313(35) 121(18) 87(100)
58	Me of 54	H	H	H	OAc	Ac	400	EI	400(14) 294(25) 252(30) 210(65) 209(100) 107(98) 43(72)
								CI	401(74) 400(8) 343(56) 342(30) 341(100)
59	Ref 2	H	OMe	H	OH	H	346	EI	346(3) 210(100) 209(15) 137(41) 94(16) 77(17)
								CI	347(13) 329(10) 210(8) 209(17) 137(100)
60	Me of 59	H	OMe	H	OMe	Me	374	EI	374(16) 343(1) 223(31) 152(25) 151(100)
								CI	375(11) 374(4) 373(2) 343(14) 151(100)
61	Me of 59	H	OMe	H	O(CH$_2$)$_4$OMe	Me	446	EI	446(3) 343(2) 209(8) 151(100) 87(77) 45(34)
								CI	
62	Me of 59	H	OMe	H	OMe	(CH$_2$)$_4$OMe	446	EI	446(2) 342(14) 223(23) 87(100) 45(23)
								CI	
63	Ref 2	H	OMe	Me	OH	H	360	EI	360(1) 210(100) 209(25) 208(30) 152(41) 151(82)
								CI	361(3) 343(3) 209(88) 151(100)
64	Rx c	p-MeOPhCH$_2$	OMe	H	OMe	Me	494	EI	494(2) 271(100) 239(4) 223(7)
								CI	
65	Rx c	3,4-diMeOPhCH$_2$	H	H	OMe	Me	494	EI	494(4) 271(100) 239(5) 223(11) 151(16)
								CI	
66	Rx c	3,4-diMeOPhCH$_2$	OMe	H	OMe	Me	524	EI	524(3) 301(100) 269(12) 223(10)

An extremely interesting fragment has been observed for the free phenolic (underivatized) adduct. An even-ion mass corresponding to loss of a benzyl group minus one of its hydrogens has been interpreted in the following way: (eq. i)
The proton-NMR spectra of the adducts strongly suggests the existence of folded-over conformations, such as in 70;[2,9] the mass spectra lend added support for this postulate.

The fragmentation which expels a quinonemethide (72) was only seen for the phenolic adducts. Apparently, the energetics are unfavorable for the transfer of methyl groups (for the derivatized adducts) to give analogous fragments. The dibenzyl adduct 52 displayed even-ion fragments at m/e 300 and 194 corresponding to the loss of two quinonemethide units (72, $R_2 = R_3 = H$, mass 106); possibly, after the first QM loss to give fragment m/e 300, structure 71, re-enolization occurs and the process is repeated again.

The mass spectrum of AHQ has never been reported. This is probably due to its great reactivity in air. If one substracts the m/e 316, 209 and 107 signals from the mass spectrum of 54, the remaining spectrum will probably be that of AHQ, namely a strong 210 signal and lesser signals at m/e 181, 152, and 77. For comparison, AQ displayed the following spectrum, m/e (%): 208(100), 207(16), 180(66), 152(43), 151(25), 150(12), and 77(27). The loss of 28 units from either the molecular ion, M - 1 ion or fragments probably corresponds to loss of CO. Anthrone shows similar losses: 194(100), 193(32), 165(77), and 82(23). The 28 unit difference also occurs in some of the adduct spectra, especially the m/e 193/165 pair.

The larger the size of the quinonemethide structural unit of the adducts, the greater the fragmentation towards benzyl ions (equation h). The spectra of dimer quinonemethide adducts 64-66 are dominated by M - 223 benzyl ions, m/e 271 or 301.

The analysis of complex mixtures can be simplified by performing selective ion monitoring of the aryl and benzyl fragments 68 and 69; this technique is shown for the reaction outlined by

equation d, where aryl fragments m/e 223 and benzyl ions m/e 121 and 151 are monitored (Figure 1). The signal at 9.5 min corresponds to QM-AHQ adduct 56 (mol. wt. 344, fragments 223 and 121). The one at 10.8 min is adduct 60 (mol. wt. 374, fragments 223 and 151). Several of the signals in Figure 1 are due to quinonemethide condensation products; the signal at 31.2 min and subsequent ones are due to diQM-AHQ adducts.

The location of $MeO(CH_2)_4$- groups in 61 and 62 was easily deduced from the appearance of a m/e 151 ion in the one case and a m/e 223 in the other. This again shows the importance of C_{10}-benzyl fragmentation process (equation h). The diacetate derivative 58, which has been fully characterized by other means, was the only compound that did not show this type of fragmentation. Its spectrum appears to be a successive loss of acetate groups as ketene (CH_2CO) and then a spectrum somewhat similar to the underivatized analog 54.

Derivatization By-Products

The method which we chose to derivatize our products prior to GC/MS analysis was that of treating the sample, dissolved in THF, with $NaOH/Me_2SO_4$. This method has been used extensively for derivatizing carbohydrates.[20] Its advantage over diazomethane is that aliphatic hydroxyl groups are also derivatized, leading to more volatile products. Its disadvantages are that the alkaline conditions can lead to undesirable sample decomposition and, as we shall show, to by-products incorporating a unit of THF between the hydroxyl group and the methyl group to be added.

In our discussion in the previous two sections, we have described compounds containing $-O(CH_2)_4OCH_3$ groups. These compounds, produced in minor amounts, probably arise by the reaction shown in equation j. These mass spectra characteristically show intense m/e 87 (73) and 45 ($MeOCH_2^+$) ions. Significant ions also occur at M - 87, M - 103 or M - 104 ($HOCH_2CH_2CH_2CH_2OMe$); see spectra for compounds 15, 16, 57, 61, and 62.

Selective ion monitoring of a product mixture can clearly show which components are THF derived; an example is given in Figure 2 of selective ion monitoring the m/e 87 ion for the THF derived components produced from the reaction outlined by equation d.

Based on our experience, the incorporation of the THF during derivatization occurs to a much greater extent with aliphatic, rather than phenolic, hydoxyl groups. This is probably a result of the aliphatic hydroxyl group's lower acidity and, therefore, slower rate of reaction.

EXPERIMENTAL

The HP 5985 GC/MS equipment and techniques were explained in the previous paper.[1] The reactions giving rise to the various products discussed here have been described elsewhere.[1-3] Samples of vanillin, vanillyl alcohol, anthrone, and anthraquinone were purchased from Aldrich Chemical Company, Milwaukee, Wisconsin.

REFERENCES

1. D. R. Dimmel, D. Shepard, and T. A. Brown, J. Wood Chem. Technol., 1, __(1981).
2. D. R. Dimmel, D. Shepard, T. A. Brown, and R. D. McKelvey, Canadian Wood Chem. Sym., Harrison Hot Springs, B. C., Canada, September 1979. Manuscript under preparation.
3. D. R. Dimmel and D. Shepard, Amer. Chem. Soc. National Meeting (Cellulose Division), Las Vegas, August 1980. Manuscript under preparation.
4. F. H. Field, Accounts Chem. Res., 1, 42 (1968).
5. M. S. B. Munson, Anal. Chem., 43 (13), 28A (1971).
6. H. Budzikiewicz, C. Djirassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holder Day, San Francisco, 1964, p. 163.
7. B.-H. Yoon, M. Okada, S. Yasuda, and N. Terashima, J. Jap. Wood Res. Soc., 25, 302 (1979).
8. J. A. Hemmingson and G. Leary, Aust. J. Chem., 33, 917 (1980).

9. L. L. Landucci, Tappi, 63(7), 95(1980); Amer. Chem. Soc. National Meeting (Cellulose Division), Las Vegas, August, 1980.

10. J. Gierer, O. Lindeberg, and I. Noren, Holzforschung, 33, 213 (1979).

11. H. Aminoff, G. Brunow, G. E. Mitsche, and K. Poppius, Paperi Puu, 61, 441 (1979).

12. I. Gourange, R. Cassidy, and C. W. Dence, Tappi, 62(7), 43(1979).

13. B. I. Fleming, G. J. Kubes, J. M MacLeod, and H. I. Bolker, Tappi, 62(7), 55(1979).

14. W. H. Algar, A. Farrington, B. Jessup, P. F. Nelson, and N. Vanderhoek, Appita, 33, 33 (1979).

15. B. F. Hrutfiord, W. T. McKean, and D. Hansen, Amer. Chem. Soc. National Meeting (Cellulose Div.), Honolulu, April 1979.

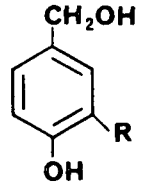
16. C. A. Eastwood, EUCEPA Sympos., Helsinki, June, 1980.

17. T. J. Fullerton and S. P. Ahern, J.C.S. Chem. Comm., 457 (1979).

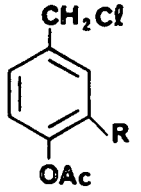
18. D. W. Cameron and E. L. Samuel, Tetrahedron Lett., 3035 (1979).

19. J. J. Fullerton and B. I. Fleming, Svensk Papperstid., 83, 396 (1980).

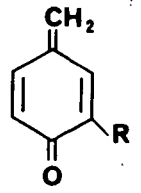
20. R. L. Whistler and M. L. Wolfrom (Editors), "Methods in Carbohydrate Chemistry," Vol. 2, Academic Press, N. Y., 1963, p. 148.



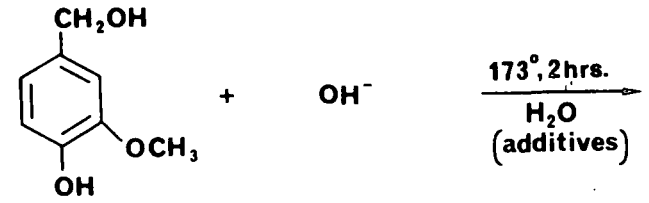
1, R = OMe
2, R = H



3, R = OMe
4, R = H

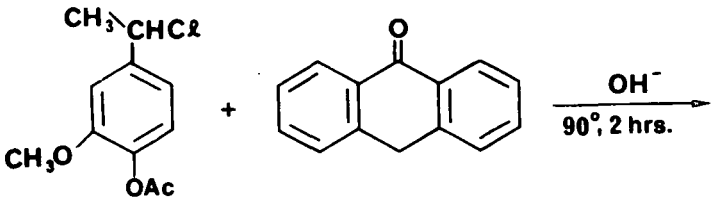


5, R = OMe
6, R = H


CH2OH
OCH3
OH
+
OH⁻
173°, 2hrs.
H2O
(additives)

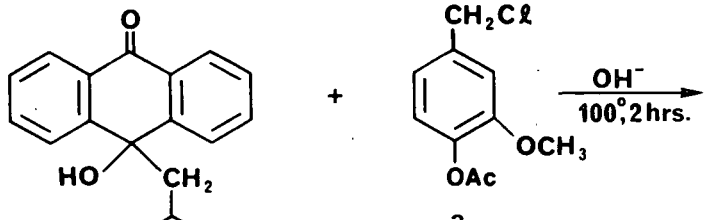
(a)

1


CH3
CHCl
CH3O
OAc
O
+
OH⁻
90°, 2 hrs.

(b)

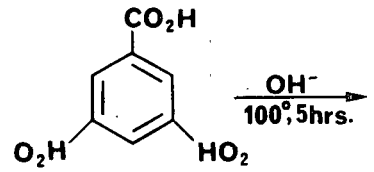
7 8


O
HO
CH2
OH
+
CH2Cl
OCH3
OAc
OH⁻
100°, 2hrs.

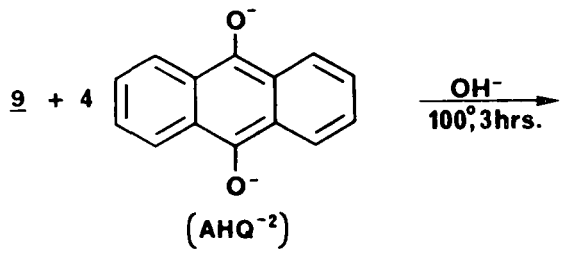
(c)

3

9


9
+
CO2H
O2H
HO2
OH⁻
100°, 5hrs.

(d)


9 + 4
O⁻
O⁻
OH⁻
100°, 3hrs.
(AHQ⁻²)

(e)

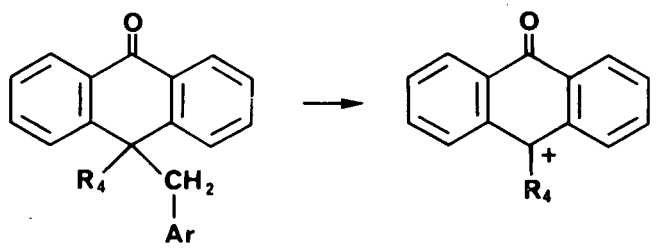
$$Cpd + A^+ \longrightarrow Cpd{-}A^+ \qquad \textbf{(f)}$$

for A = H, M + 1

A = C_2H_5, M + 29

A = C_3H_5, M + 41

$$Frag{-}OR + A^+ \longrightarrow \underset{(M-OR)}{Frag^+} + AOR \qquad \textbf{(g)}$$



(h)

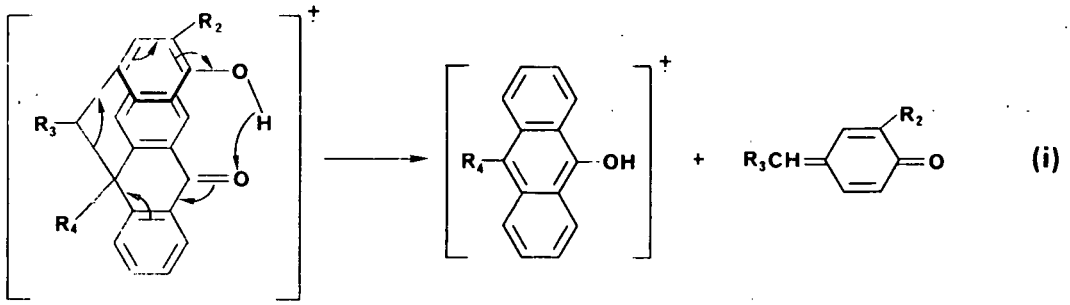
67

68

69

m/e 193, R_4 = H
m/e 209, R_4 = OH
m/e 223, R_4 = OMe

m/e 107
m/e 121
m/e 137
m/e 151
m/e 165



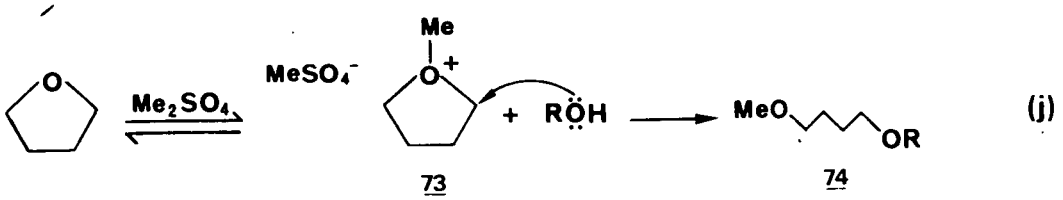
(i)

70

71

72

m/e 194, R_4 = H
m/e 210, R_4 = OH
m/e 300, R_4 = p-HOPhCH_2

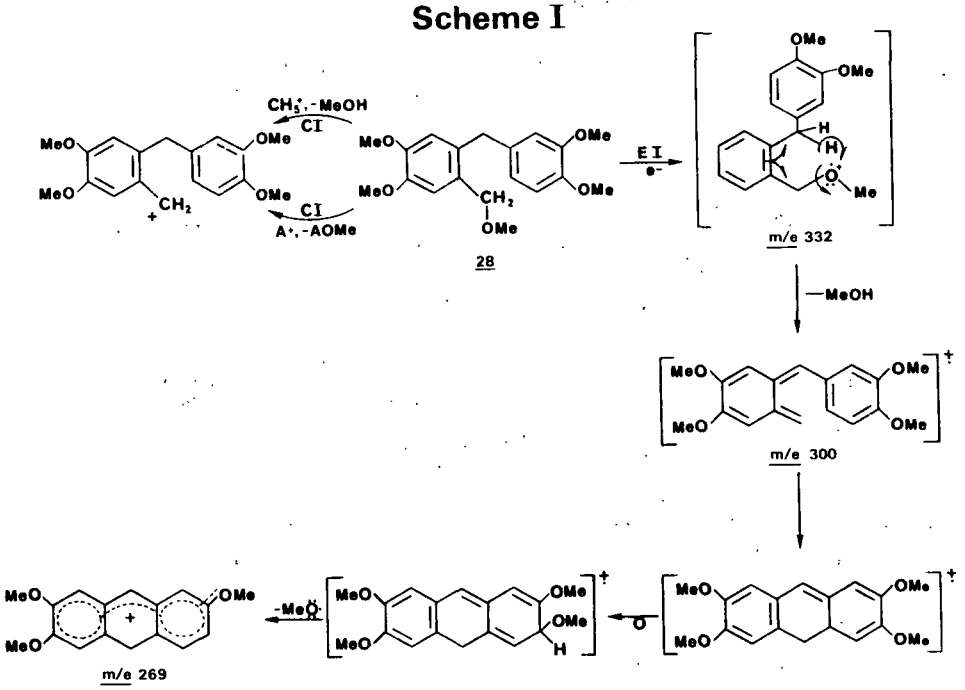


(j)

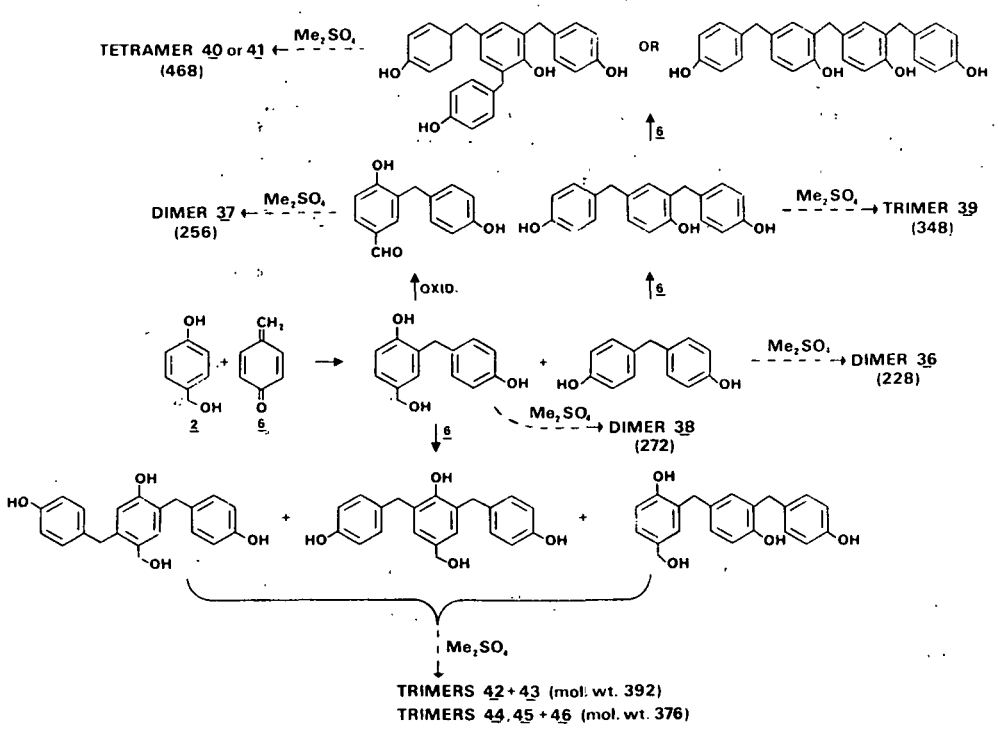
73

74

Scheme I



Scheme II


TETRAMER 40 or 41
(468)
Me2SO4
OR
DIMER 37
(256)
TRIMER 39
(348)
OXID.
DIMER 36
(228)
DIMER 38
(272)
TRIMERS 42 + 43 (mol. wt. 392)
TRIMERS 44, 45 + 46 (mol. wt. 376)

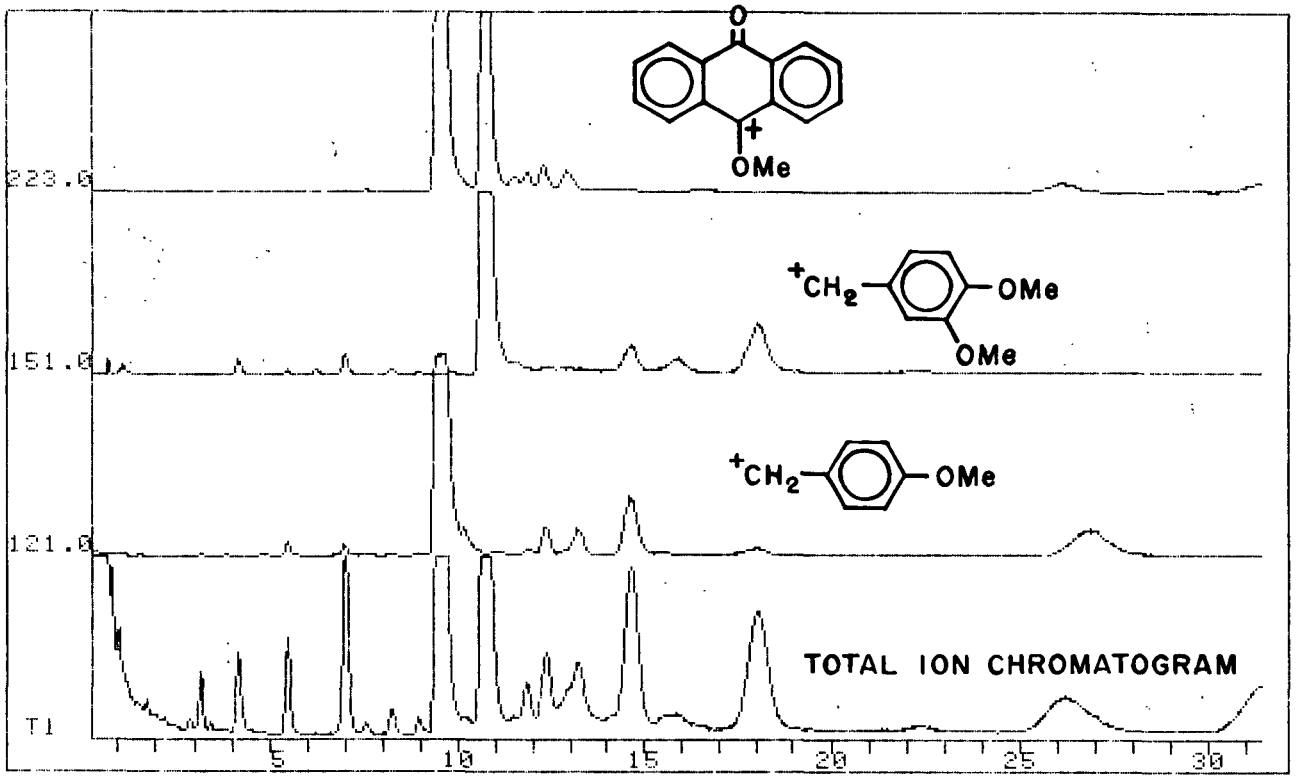


Figure 1. Partial display of the total ion chromatogram and selective ion monitoring for the products of the reaction described by equation d, after derivatization. The Y-scale has been expanded by a factor of four to more graphically display the minor components.

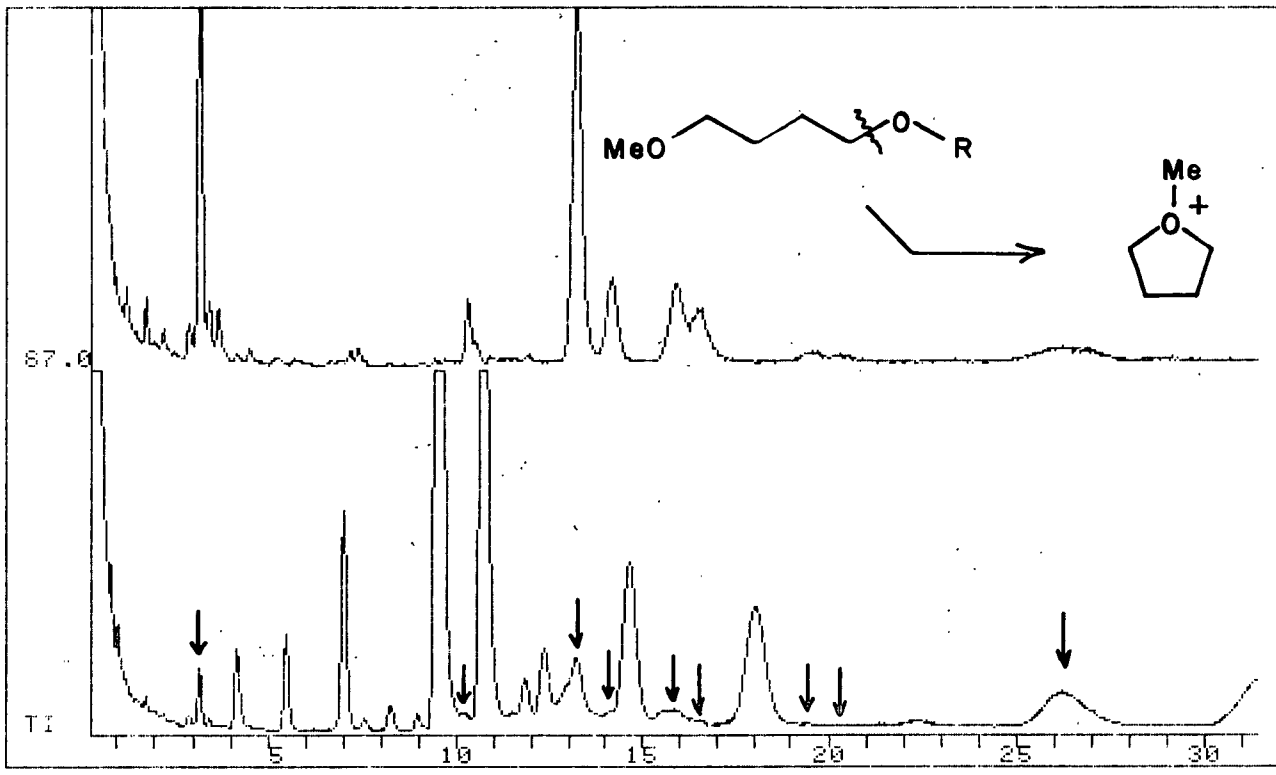


Figure 2. Partial display of the total ion chromatogram and selective ion monitoring of m/e 87 for the products of the reaction described by equation d, after derivatization. The arrows on the lower trace are THF derived products.